UNITED
NATIONS

ST

Secretariat

Distr.
GENERAL

ST/SG/AC.10/C.3/1997/81
1 October 1997

Original: ENGLISH

COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fourteenth session,
Geneva, 8-18 December 1997,
agenda item 2 (d))

DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Other draft amendments

Toxic by inhalation substances

Transmitted by the Expert from the United States of America

Introduction

1. During the thirteenth session, the Sub-Committee favorably received conceptual proposals for including in the Model Regulations special requirements for substances that are toxic by inhalation (TIH substances) as presented in SG/AC.10/C.3/1997/20. Conceptual proposals in that paper had the intent of improving the hazard communication of these substances for purposes of transport acceptance and emergency services personnel, and improving the packaging of such materials to reduce the likelihood of release in transport. The purpose of this paper is to recommend specific requirements for improving hazard communication with respect to these substances. Packaging changes will be addressed in a comprehensive proposal expected to be submitted to the fifteenth session.

Definition of TIH substances

2. TIH substances are considered to be either liquid substances having vapours that meet the criteria for Division 6.1 on the basis of their inhalation toxicity or Division 2.3 substances. Further, it is proposed that only those substances meeting the Div. 6.1 Packing Group I criteria should be considered as TIH substances.

Division 6.1 substances that are assigned to Packing Group II or III are considered to be less dangerous owing to their lower volatility and lower toxicity and special hazard communication for those substances is not considered to be warranted. Substances that are toxic by inhalation of dusts and mists are also not included.

Note: For purposes of assigning packaging requirements, it is also proposed that TIH substances of Div. 6.1 be subdivided into two groups according to their degree of toxicity. Under the harmonization of classification criteria agenda item, the Committee has supported the OECD proposal to provide an inhalation toxicity breakpoint of 250 ml/m^3. It is proposed that this breakpoint be used to subdivide Division 6.1 substances and that consistent with the approach already taken in the Regulations that a minimum vapor pressure be associated with this breakpoint. It is proposed that Packing Group I be subdivided into two groups as follows:

Group IA - substances with an inhalation toxicity of 250 ml/m^3 or less and $V > 500LC_{50}$; and

Group IB - substances with an inhalation toxicity of more than 250 ml/m^3 and less than or equal to 1000 ml/m^3 and $V > 10LC_{50}$

However, this distinction is not considered necessary for purposes of hazard communication.

NOS Proper shipping names

3. In order that Div. 6.1 TIH substances that are transported under NOS proper shipping names can be distinguished from other Div 6.1 substances, it is proposed that new NOS descriptions for these substances be developed. It is proposed that this distinction be made through the inclusion of the words "Toxic by Inhalation" in each new shipping name. The following new entries are proposed:

(2)	(3)	(4)	(5)	(6)	(7)
TOXIC BY INHALATION LIQUID, ORGANIC, N.O.S.	6.1		I	109 274 xxx	NONE
TOXIC BY INHALATION LIQUID, INORGANIC, N.O.S.	6.1		I	109 274 xxx	NONE
TOXIC BY INHALATION LIQUID, FLAMMABLE, ORGANIC, N.O.S.	6.1	3	I	109 274 xxx	NONE
TOXIC BY INHALATION LIQUID, WATER-REACTIVE, N.O.S.	6.1	4.3	I	109 274 xxx	NONE
TOXIC BY INHALATION LIQUID, OXIDIZING, N.O.S.	6.1	5.1	I	109 274 xxx	NONE
TOXIC BY INHALATION LIQUID, CORROSIVE, ORGANIC, N.O.S.	6.1	8	I	109 274 xxx	NONE
TOXIC BY INHALATION LIQUID, CORROSIVE, INORGANIC, N.O.S.	6.1	8	I	109 274 xxx	NONE

Each of these entries should have the following special provision indicated in column 6 of the Dangerous Goods list:

> "XXX This entry shall only be used for Division 6.1 substances that meet the inhalation toxicity criteria for packing group I described in 2.6.2.2.4.3."

4. To prevent existing liquid toxic substance NOS entries from being used to transport TIH substances, a special provision indicating that those entries should not be used if the substance meets the TIH criteria should be placed against each such toxic NOS entry which would no longer be appropriate for TIH substances. The new special provision should read:

> "YYY This entry shall not be used for Division 6.1 substances that meet the inhalation toxicity criteria for packing group I described in 2.6.2.2.4.3."

This special provision should appear in column 6 of the Dangerous Goods List against the following entries:

> 2810, 2927, 2929, 3122, 3123, 3287, and 3289.

Labelling and Placarding

5. To convey the special dangers that TIH substances pose, it is also proposed that TIH substances be identified through a special label and placard. The expert from the United States considers that a label distinct from the Division 6.1 label is necessary in order to effectively communicate the risk of TIH substances to emergency response personnel. Proposed labels for TIH substances and gases are shown in Annex 1. While the proposed labels do not pictorially convey the toxic by inhalation hazard they are visible from long distances and they are clearly distinct from the label used for other toxic substances. As such they will enable *trained* emergency services personnel to recognize the special hazard the labels are intended to convey.

6. It is proposed that the class 2.3 label shown in Annex 1 replace label No. 2.3 in 5.2.2.2.2.1 and that the existing No.6.1 label would be redescribed as:

(No. 6.1A)
Division 6.1
Toxic substances other than packing group I toxic by inhalation substances

The Division 6.1 label shown in Annex 1 would be added to 5.2.2.2.2.1 as an additional label with the following description:

(No. 6.1B)
Division 6.1
Packing group I toxic by inhalation substances

Documentation

7. In the case of substances transported under new NOS descriptions, the fact that a substance is a TIH substance will be clear from the proper shipping name that is used. In the case of Division 2.3 gases, it will be clear from the 2.3 Division indicated in the basic description. However, for substances transported under specific shipping names, no information currently required to be provided on the shipping paper conveys the information that the substance is a TIH substance. It is proposed that on shipping papers listing TIH substances under a specific chemical proper shipping name that the words

"Toxic by Inhalation" be required to be placed on the shipping paper immediately after the basic description.

8. It is proposed that a new paragraph 5.4.1.1.6 be added (existing 5.4.1.1.6 and subsequent paragraphs renumbered) as follows:

"5.4.1.1.6 *Special provision for Division 6.1 toxic by inhalation substances*

For Division 6.1 substances that meet the inhalation toxicity criteria for packing group I (see 2.6.2.2.4.3) that are described on the transport document by a proper shipping name that does not convey that the substance is toxic by inhalation, the words "Toxic by Inhalation" shall be placed immediately following the basic description required by 5.4.1.1.1."

Identification of Substances Meeting the Inhalation Criteria Division 6.1, Packing Group I

9. To identify those named substances to which the proposed new Division 6.1 label, and the proposed transport document provision should apply, it is proposed that a new special provision be added in column 6 of the Dangerous Goods List as follows:

> "ZZZ This substance is considered to meet the inhalation criteria of Division 6.1, Packing Group I. Model No. 6.1B labels and placards shall be used and the substance must be described on the transport document in accordance with 5.4.1.1.6."

10. Substances which the expert from the United States considers as meeting these criteria and the basis for this classification are provided in Annex 2. It is proposed that special provision ZZZ be placed against each of these substances independent of whether the substance is currently assigned to Division 6.1.

* * * * *

Annex 1

LABEL

Annex 2

List Of Substances in the United Nations' Dangerous Goods List
known to be Toxic by Inhalation

UN NO	*MATERIAL*	*LC50 (ppm)*	*LCLo (ppm)*	*NOTE*	*VP (20 °C) (ppm)*	*NOTE*	*RTECS***	*GROUP*
UN 1541	Acetone cyanohydrin, stabilized	--	126	R*	13200		OD9275	B
UN 1092	Acrolein, inhibited	25	--	D	289000		AS1050	A
UN 1098	Allyl alcohol	253	--	R*	26000		BA5075	B
UN 2334	Allylamine	590	--	R*	261000		BA5425	B
UN 1722	Allyl chloroformate	61	--	C	20400		LQ5775	B
UN 1560	Arsenic trichloride	--	56	R*m	11500		CG1750	B
UN 2692	Boron tribromide	--	--	1	73700		ED7400	B
UN 1744	Bromine	113	--	R*m	237000		EF9100	A
UN 1744	Bromine solutions	--	--	14	--		EF9100	+
UN 1745	Bromine pentafluoride	--	50	eS	453000		EF9350	A
UN 1746	Bromine trifluoride	50	--	eS	9200		EF9360	B
UN 1569	Bromoacetone	--	95	R*h	11900		UC0525	B
UN 2743	n-Butyl chloroformate	--	--	1	9870		LQ5890	B
UN 2485	n-Butyl isocyanate	105	--	C	13900		NQ8250	B
UN 2484	tert-Butyl isocyanate	22	--	A	19700		NQ8300	A
UN 1695	Chloroacetone, stabilized	262	--	R	41900		UC0700	B
UN 2668	Chloroacetonitrile	--	500	R*	13200		AL8225	B
UN 1752	Chloroacetyl chloride	660	--	C	24600		AO6475	B

UN NO	MATERIAL	LC50 (ppm)	LCLo (ppm)	NOTE	VP (20 °C) (ppm)	NOTE	RTECS**	GROUP
UN 2232	2-Chloroethanal (Chloroacetaldehyde)	160	--	A	24300		AB2450	B
UN 1580	Chloropicrin	--	50	R*h	26100		PB6300	B
UN 1583	Chloropicrin mixtures, n.o.s.	--	--	14	--		PB6320	+
UN 1754	Chlorosulfonic acid	16	--	C	1320	25 °C	FX5730	B
UN 1143	Crotonaldehyde, stabilized	93	--	R*	42100		GP9499	B
UN 2488	Cyclohexyl isocyanate	15	--	A	2170		NQ8650	B
UN 2521	Diketene, inhibited	551	--	A	10500		RQ8225	B
UN 2382	Dimethylhydrazine, symmetrical	680	--	C*	92000	25 °C	MV2625	B
UN 1163	Dimethylhydrazine, unsymmetrical	504	--	R*	206000	25 °C	MV2450	B
UN 1595	Dimethyl sulfate	17	--	R*	1000		WS8225	B
UN 1182	Ethyl chloroformate	145	--	R	55300		LQ6125	B
UN 2826	Ethyl chlorothioformate	138	--	C	10900		LQ6950	B
UN 1892	Ethyldichloroarsine	36	--	R*	2800		CH3500	B
UN 1135	Ethylene chlorohydrin	74	--	A	6450		KK0875	B
UN 1605	Ethylene dibromide	650	--	A	11300		KH9275	B
UN 1185	Ethyleneimine, inhibited	76	--	R*	217000		KX5075	A
UN 2481	Ethyl isocyanate	--	--	14	--		NQ8825	A
UN 2646	Hexachlorocyclopentadiene	3	--	R*	100		GY1225	B
UN 1613	Hydrocyanic acid, aqueous solutions	--	--	14	--		MW6840	B
UN 3294	Hydrogen cyanide, solution in alcohol	--	--	14	--		--	+
UN 1051	Hydrogen cyanide, stabilized	40	--	R*	842000		MW6825	A
UN 1614	Hydrogen cyanide, stabilized (absorbed)	--	--	14	--		--	+
UN 1052	Hydrogen fluoride, anhydrous	1300	--	CGA	1020000		MW7875	C

ST/SG/AC.10/C.3/1997/81
page 7
Annex 2

UN NO	MATERIAL	LC50 (ppm)	LCLo (ppm)	NOTE	VP (20 C) (ppm)	NOTE	RTECS**	GROUP
UN 1994	Iron pentacarbonyl	6	--	R*	30300		NO4900	A
UN 2486	Isobutyl isocyanate	--	--	14	--		NQ9208	A
UN 2407	Isopropyl chloroformate	299	--	A	36800		LQ6475	B
UN 2483	Isopropyl isocyanate	--	--	14	--		NQ9230	A
UN 3281	Metal carbonyls, n.o.s.	--	--	14	--		--	+
UN 3079	Methacrylonitrile, inhibited	656	--	R*	84200		UD1400	B
UN 3246	Methanesulfonyl chloride	205	--	A	2760		--	B
UN 2605	Methoxymethyl isocyanate	--	--	14	--		NQ9240	A
UN 1647	Methyl bromide and Ethylene dibromide mixtures, liquid	--	--	14	--		PA5300	B
UN 1238	Methyl chloroformate	88	--	R	135000		FG3675	A
UN 1239	Methyl chloromethyl ether	160	--	R*	210000		KN6650	A
UN 1244	Methylhydrazine	68	--	R*	50300		MV5600	A
UN 2644	Methyl iodide	448	--	R*	414000		PA9450	B
UN 2480	Methyl isocyanate	22	--	A*	458000		NQ9450	A
UN 2477	Methyl isothiocyanate	635	--	C	27400		PA9625	B
UN 2606	Methyl orthosilicate	200	--	C	13300		VV9800	B
UN 1251	Methyl vinyl ketone	5	--	C*	93400		EM9800	A
UN 1259	Nickel carbonyl	18	--	R*	422000		QR6300	A
UN 2032	Nitric acid, red fuming (NO2)	134	--	R*	55300		QU5900	B
UN 3275	Nitriles, toxic, flammable, n.o.s.	--	--	14	--		--	+
UN 3276	Nitriles, toxic, n.o.s.	--	--	14	--		--	+
UN 3023	tert-Octyl mercaptan	102	--	R*	5000		MJ1500	B

UN NO.	MATERIAL	LC50 (ppm)	LCLo (ppm)	NOTE	VP (20 C) (ppm)	NOTE	RTECS**	GROUP
UN 3280	Organoarsenic compound, n.o.s.	--	--	14	--		--	+
UN 3279	Organophosphorus compound, toxic, flammable, n.o.s.	--	--	14	--		--	+
UN 3278	Organophosphorus compound, toxic, n.o.s.	--	--	14	--		--	+
UN 1380	Pentaborane	12	--	R*	225000		RY8925	A
UN 1670	Perchloromethyl mercaptan	--	69	R*	32900		PB0370	B
UN 1672	Phenylcarbylamine chloride	--	1	20000		e	NJ6700	B
UN 2487	Phenyl isocyanate	16	--	A	2470		DA3675	B
UN 2337	Phenyl mercaptan	66	--	R*	1450		DC0525	B
UN 1810	Phosphorus oxychloride	96	--	R*	35500		TH4897	B
UN 1809	Phosphorus trichloride	208	--	R*	125000		TH3675	B
UN 2927	Poisonous liquids, corrosive, n.o.s.	--	--		--		--	+
UN 2929	Poisonous liquids, flammable, n.o.s.	--	--		--		--	+
UN 2810	Poisonous liquids, n.o.s.	--	--		--		--	+
UN 3122	Poisonous liquids, oxidizing, n.o.s.	--	--		--		--	+
UN 3123	Poisonous liquids which in contact with water emit flammable gases, n.o.s.	--	--		--		--	+
UN 2740	n-Propyl chloroformate	319	--	Rm	25500		LQ6830	B
UN 2482	n-Propyl isocyanate	44	--	A	69700		NR0190	A
UN 1828	Sulfur chloride (mono)	327	--	C	8950		WS4300	B
UN 1829	Sulfur trioxide, inhibited	347	--	C	98700		WT4830	B
UN 1831	Sulfuric acid, fuming (=, >30% free SO3)	347	--	R	=, >3470		WS5605	B
UN 1834	Sulfuryl chloride	131	--	C	142000		WT4870	A
UN 1510	Tetranitromethane	36	--	R*	11000		PB4025	B

ST/SG/AC.10/C.3/1997/81
Page 9
Annex 2

UN NO	MATERIAL	LC50 (ppm)	LCLo (ppm)	NOTE	VP (20°C) (ppm)	NOTE	RTECS**	GROUP
UN 2474	Thiophosgene	--	--	I	150000		XN2450	B
UN 1838	Titanium tetrachloride	119	--	R*	12800		XR1925	B
UN 3289	Toxic liquid, corrosive, inorganic, n.o.s.	--	--	--	--		--	+
UN 2927	Toxic liquid, corrosive, organic, n.o.s.	--	--	--	--		--	+
UN 2929	Toxic liquid, flammable, organic, n.o.s.	--	--	--	--		--	+
UN 3287	Toxic liquid, inorganic, n.o.s.	--	--	--	--		--	+
UN 2810	Toxic liquid, organic, n.o.s.	--	--	--	--		--	+
UN 3122	Toxic liquid, oxidizing, n.o.s.	--	--	--	--		--	+
UN 3123	Toxic liquid, water-reactive, n.o.s.	--	--	--	--		--	+
UN 2442	Trichloroacetyl chloride	128	--	R*	22700		A07140	B
UN 2438	Trimethylacetyl chloride	507	--	C	35500		AO7200	B

KEY

**	RTECS numbers are given here without the four additional zeros that appear in the actual number
I	These materials are considered to be poisonous by inhalation although no inhalation data are available
A	Data obtained from Special Approvals
C	Data obtained by GEC
E	Data obtained from the Elsevier Gas Encyclopedia
M	Data obtained from the Matheson Gas Data Book
R	Data obtained from the RTECS
e	Estimated
h	Test involved humans
m	Test involved mice
*	LC50 value converted to 1 hour
#	Use LC50 of the material to determine the group
CGA	Data supplied by the Compressed Gas Association, Inc. (CGA P-20--1995)
GROUP	See note under paragraph 2 of the main document
RTECS	Registry of Toxic Effects of Chemical Substances (NIOSH)
VP	Vapor pressure in psig at 70°F, 115°F, and 130°F, respectively
?	Time not specified.